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| (51) International Patent Classification ⁶ : C11D 3/39, 3/50, C01B 15/04, 15/055 | A1 | (11) International Publication Number: WO 96/19560 (43) International Publication Date: 27 June 1996 (27.06.96) |
| (51) International Application Number: PCT/US95/16249 (22) International Filing Date: 8 December 1995 (08.12.95) (30) Priority Data: 9425876.1 21 December 1994 (21.12.94) GB (71) Applicant (for all designated States except US): THE PROCTER & GAMBLE COMPANY [US/US]; One Procter & Gamble Plaza, Cincinnati, OH 45202 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): McRITCHIE, Allan, Campbell [GB/GB]; 35 Monkseaton Drive, Whitley Bay, Tyne & Wear NE26 1SY (GB). GREEN, Michael [GB/GB]; 69 Oulton Close, Meadow Rise Kenton, Newcastle upon Tyne NE5 4SX (GB). (74) Agents: REED, T., David et al.; The Procter & Gamble Company, 5299 Spring Grove Avenue, Cincinnati, OH 45217 (US). | | (81) Designated States: BR, CA, CN, JP, MX, US, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| (54) Title: PERFUMED BLEACHING COMPOSITIONS (57) Abstract <p>There is provided a perfumed bleaching composition containing: a-a bleaching system selected from i)-a perhydrate in amount of from 0.1 % to 60 % by weight and combined with a bleach activator in amount of from 0.1 % to 60 % by weight, ii)-a preformed peracid in amount of from 0.1 % to 60 % by weight, and any mixtures thereof, wherein said perhydrate and/or said preformed peracid are coated; and b-a perfume in amount from 0.05 % to 2 % by weight which comprises aroma chemicals selected from: primary and secondary alcohols, aliphatic aldehydes, hydrocinnamic aldehydes, esters excluding salicylates, unsaturated ketones and mixtures thereof, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 30 % by weight of the perfume. The perfumed bleaching composition also preferably comprises a chelant which further enhances the storage stability of the perfume.</p> | | |

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PERFUMED BLEACHING COMPOSITIONS

Field of the invention

The invention relates to perfumed bleaching compositions. More specifically, it relates to bleaching compositions comprising a bleach system and a stabilised perfume composition.

Background of the invention

Perfumes are an important and desirable part of detergent compositions. They are used to cover up the chemical odours of the cleaning ingredients and provide an aesthetic benefit to the wash process and, preferably the cleaned fabrics. EP 430315, which discloses the use of a laundry detergent composition containing a lipase and a perfume having specific fragrance materials, exemplifies such use. In said patent, the perfume composition is said to counteract the problem of the residual malodour of lipase treated laundry.

However, perfumes generally are volatile and many perfume ingredients can be destroyed or damaged by contact with cleaning ingredients, especially alkali and bleaches. To minimise direct contact between perfume and bleach components in granular compositions, bleaches are sometimes admixed after perfume spray-on. Even this does not avoid oxidation of perfumes by bleaches, especially bleach activator/bleaching agent combinations, at least partly because of perfume mobility in the compositions.

One solution to this problem is encapsulation of the perfume. This increases the expense and complexity of formulation and does not always provide sufficient protection. EP 332259 teaches the use of a liquid detergent composition containing peroxyacid bleach and perfumed silica particles which protect the perfume from oxidation by the bleach.

Despite the above disclosures, there is a continuing need for the development or identification of perfumes suitable for use in bleaching compositions containing a bleach system selected from a perhydrate in combination with a bleach activator and a preformed peracid.

Coating the bleaching agent in order to stabilise it has been extensively disclosed in the patent literature, an example being WO 94/01521 which describes the use of a detergent composition comprising a bleach activator, a coated alkali metal percarbonate bleach wherein the coating material is a mixed salt of an alkali metal carbonate and alkali metal sulphate, a chelant (EDDS) and a perfume.

It has now been found that coating the source of active oxygen such as the perhydrate and/or the preformed peracid allows the use of new perfume compositions.

It has also been found that the further coating of the bleach activator allows the use of such new perfume compositions.

Therefore, it is an object of the invention to provide a perfume composition comprising aroma chemicals selected from primary and secondary alcohols, aliphatic aldehydes, hydrocinnamic aldehydes, esters excluding salicylates and unsaturated ketones in a bleaching composition containing a bleaching system, selected from a perhydrate in combination with a bleach activator and a preformed peracid wherein said perhydrate and/or said preformed peracid are coated, which gives an excellent perfume fragrance on fabrics as well as an excellent perfume stability in presence of the bleaching ingredient in the wash liquor and in the product during storage.

For the purpose of the present invention, a perfumed bleaching composition consists of a bleaching composition and a perfume composition, both as defined hereinafter, wherein said perfume is incorporated by any means in a composition selected from:

- i)-the bleaching composition as a finished product,
- ii)-the bleaching composition during its making process,

or any mixtures thereof.

Processes for incorporating the perfume in the bleaching composition are not critical to the present invention. This can be done by spray-on, admixture with one or more component of the bleaching composition or other means known to the man skilled in the art. A preferred process, for cost and practicability reasons, is a spray-on process.

Summary of the invention

The present invention relates to a perfumed bleaching composition containing:

a-a bleaching system selected from

i)-a perhydrate in amount of from 0.1% to 60% by weight and combined with a bleach activator in amount of from 0.1% to 60% by weight,

ii)-a preformed peracid in amount of from 0.1% to 60% by weight,

and any mixtures thereof,

wherein said perhydrate and/or said preformed peracid are coated; and

b-a perfume in amount from 0.05% to 2% by weight which comprises aroma chemicals selected from: primary and secondary alcohols, aliphatic aldehydes, hydrocinnamic aldehydes, esters excluding salicylates, unsaturated ketones and mixtures thereof, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 30% by weight of the perfume.

In preferred embodiments of the invention, the bleaching composition may comprise a coated bleach activator and/or a chelant such as EDDS which further enhances the storage stability of the perfume.

Detailed description of the invention

The present invention contemplates bleaching compositions having an excellent perfume fragrance as well as an excellent perfume stability.

More particularly, it relates to a perfumed bleaching composition containing:

a-a bleaching system selected from

i)-a perhydrate in amount of from 0.1 % to 60% by weight and combined with a bleach activator in amount of from 0.1 % to 60% by weight,

ii)-a preformed peracid in amount of from 0.1 % to 60% by weight,

and any mixtures thereof,

wherein said perhydrate and/or said preformed peracid are coated; and

b-a perfume in amount from 0.05 % to 2% by weight which comprises aroma chemicals selected from: primary and secondary alcohols, aliphatic aldehydes, hydrocinnamic aldehydes, esters excluding salicylates, unsaturated ketones and mixtures thereof, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 30% by weight of the perfume.

Bleaching System

The compositions according to the present invention herein contain bleaching agents or bleaching compositions containing a bleaching system, selected from a perhydrate in combination with one or more bleach activators and one or more preformed peracids wherein said perhydrate and/or said preformed peracid are coated. When present, bleaching agents will typically be at levels of from 0.1 % to 60%, more typically from 1 % to 30%, and more preferably from 5 % to 20% of the bleaching composition, especially for fabric laundering.

The bleaching agents used herein can be any of the bleaching agents useful for detergent compositions in textile

cleaning, hard surface cleaning, or other cleaning purposes that are now known or become known. The bleaching agent, source of alkaline hydrogen peroxide in the wash liquor, is an inorganic perhydrate bleach or a preformed peracid.

The perhydrate may be any of the alkali inorganic salts such as perborate monohydrate or tetrahydrate, percarbonate, perphosphate and persilicate salts, but is conventionally an alkali metal perborate or percarbonate.

Sodium percarbonate, which is the preferred perhydrate, is an addition compound having a formula corresponding to $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Most commercially available material includes a low level of a heavy metal sequestrant such as EDTA, 1-hydroxyethylene 1,1-diphosphonic acid (HEDP) or an aminophosphonate, that is incorporated during the manufacture process.

Another category of bleaching agent that can be used in place of or in combination with the mixture of a coated perhydrate and a bleach activator encompasses the preformed peracid bleaching agents and salts thereof. Suitable examples of this class of agents include (6-octylamino)-6-oxo-caproic acid, (6-nonylamino)-6-oxo-caproic acid, (6-decylamino)-6-oxo-caproic acid, magnesium monoperoxyphthalate hexahydrate, the magnesium salt of metachloro perbenzoic acid, 4-nonylamino-4-oxoperoxybutyric acid and diperoxydodecanedioic acid. Such bleaching agents are disclosed in U.S. Patent 4,483,781, U.S. Patent 4,634,551, EP 0,133,354, U.S. Patent 4,412,934 and EP 0,170,386.

Mixtures of bleaching agents can also be used.

An essential component of the invention is a coating for the bleaching agent which prevents the source of damage (hydrogen peroxide (H_2O_2) and/or peroxide anion) from diffusion such that less than 5% of the peroxide source is diffused upon storage. Thereby, the present invention provides an enhancement in the perfume stability after a minimum of 24 hours storage of at least

1 panel grade, preferably 2 panel grades, after grading conducted by an expert panel. The stability grade is given versus a laboratory prepared standard product (grade 10.0) on a 1 to 10 scale. The bleach agent coating material can be selected from mixtures of alkali metal sulphate and carbonate, sodium silicate, borate and water-soluble surfactant. The bleaching agent is preferably percarbonate. The most preferred coating material comprises mixed salt of an alkali and/or alkaline earth metal sulphate and carbonate.

Such coatings together with coating processes have previously been described in GB-1,466,799. The weight ratio of the mixed salt coating material to the bleaching agent lies in the range from 1 : 200 to 1 : 4, more preferably from 1 : 99 to 1 : 9, and most preferably from 1 : 49 to 1:19. Preferably, the mixed salt is of sodium sulphate and sodium carbonate which has the general formula $\text{Na}_2\text{SO}_4 \cdot n \cdot \text{Na}_2\text{CO}_3$ wherein n is from 0.1 to 3, preferably n is from 0.3 to 1.0 and most preferably n is from 0.2 to 0.5.

Another suitable coating material is sodium silicate of SiO_2 : Na_2O ratio from 1.6 : 1 to 3.4 : 1, preferably 2.8 : 1, applied as an aqueous solution to give a level of from 2% to 10%, (normally from 3% to 5%) of silicate solids by weight of the bleaching agent. Magnesium silicate can also be included in the coating. Also useful as bleaching agent coating materials are sodium citrate, borate or water-soluble surfactants such as linear alkyl benzene sulphonate and alkyl ether sulphate. A useful coating material for the percarbonate bleaching agent is a solid inorganic coating material consisting of a mixture of sodium carbonate and sodium chloride disclosed in EP-A-592969.

Preferred peroxygen bleaching agents selected from alkali metal perborates tetrahydrates and monohydrates and percarbonates, etc., are combined with bleach activators, which lead to the *in situ* production in aqueous solution (i.e., during the washing process) of the peroxy acid corresponding to the bleach activator.

The amount of bleach activator will typically be from 0.1 % to 60%, more typically from 0.5% to 40% by weight of the bleaching composition.

These activators preferably contain one or more N- or O-acyl groups and may be selected from a wide range of classes. Various nonlimiting examples of activators are disclosed in U.S. Patent 4,915,854 and U.S. Patent 4,412,934. The nonanoyloxybenzene sulfonate (NOBS), isononanoyloxybenzene sulfonate (ISONOBS) and tetraacetyl ethylene diamine (TAED) activators are typical, and mixtures thereof can also be used.

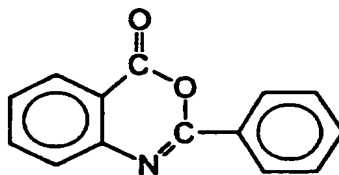
Highly preferred amido-derived bleach activators are those of the formulae:



wherein R^1 is an alkyl group containing from 6 to 12 carbon atoms, R^2 is an alkylene containing from 1 to 6 carbon atoms, R^5 is H or alkyl, aryl, or alkaryl containing from 1 to 10 carbon atoms, and L is any suitable leaving group. A leaving group is any group that is displaced from the bleach activator as a consequence of the nucleophilic attack on the bleach activator by the perhydrolysis anion. A preferred leaving group is phenyl sulfonate.

Preferred examples of bleach activators of the above formulae include (6-octanamido-caproyl)oxybenzenesulfonate, (6-nonanamidocaproyl)oxybenzenesulfonate, (6-decanamidocaproyl)oxybenzene- sulfonate, and mixtures thereof as described in U.S. Patent 4,634,551.

Another class of bleach activators comprises the benzoxazin-type activators disclosed in U.S. Patent 4,966,723. A highly preferred activator of the benzoxazin-type is:



Still another class of preferred bleach activators includes the acyl lactam activators, especially acyl caprolactams and acyl valerolactams of the formulae:


$$\begin{array}{c} \text{X}^- \\ \text{R}'' \quad \text{R}' \quad \text{R} \\ \quad \quad \quad | \\ \quad \quad \quad \text{N}^+ \\ \quad \quad \quad | \\ \quad \quad \quad \text{CH}_2 \\ \quad \quad \quad | \\ \text{---} \text{C}_6\text{H}_4 \text{---} \text{C}(=\text{O}) \text{---} \text{N} \text{---} \text{C}(=\text{O}) \text{---} (\text{CH}_2)_x \text{---} \text{CH}_2 \\ \quad \quad \quad | \quad \quad \quad | \\ \quad \quad \quad \text{CH}_2 \text{---} \text{CH}_2 \quad \quad \quad \text{CH}_2 \end{array}$$

Mixture of any of the bleach activators hereinbefore described may be used.

In a preferred embodiment, the bleach activator component is in a coated form. The coating material is selected from a mixture of

alkali metal C₈-C₂₂ fatty acid salts in admixture with the corresponding fatty acids (disclosed in GB 1507312), a coating of C₁₄-C₁₈ fatty acid mixtures (disclosed in GB 1381121), a mixture of C₁₂-C₁₄ fatty acids and C₁₀-C₂₀ aliphatic alcohols (disclosed in GB 1441416) and an organic acid coating (disclosed in WO 92/13798).

Bleaching agents other than oxygen bleaching agents are also known in the art and can optionally be utilized herein. One type of non-oxygen bleaching agent of particular interest includes photoactivated bleaching agents such as the sulfonated zinc and/or aluminium phthalocyanines. See U.S. Patent 4,033,718. If used, bleaching compositions will typically contain from 0.025% to 1.25%, by weight, of such bleaches, especially sulfonate zinc phthalocyanine.

If desired, the bleaching compounds can be catalysed by means of a manganese compound. Such compounds are well known in the art and include, for example, the manganese-based catalysts disclosed in U.S. Pat. 5,246,621, U.S. Pat. 5,244,594; U.S. Pat. 5,194,416; U.S. Pat. 5,114,606; and EP 549,271A1, 549,272A1, 544,440A2, and 544,490A1; Preferred examples of these catalysts include Mn^{IV}₂(u-O)₃(1,4,7-trimethyl-1,4,7-triazacyclononane)₂(PF₆)₂, Mn^{III}₂(u-O)₁(u-OAc)₂(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(ClO₄)₂, Mn^{IV}₄(u-O)₆(1,4,7-triazacyclononane)₄(ClO₄)₄, Mn^{III}Mn^{IV}₄(u-O)₁(u-OAc)₂-(1,4,7-trimethyl-1,4,7-triazacyclononane)₂(ClO₄)₃, Mn^{IV}(1,4,7-trimethyl-1,4,7-triazacyclononane)- (OCH₃)₃(PF₆), and mixtures thereof. Other metal-based bleach catalysts include those disclosed in U.S. Pat. 4,430,243 and U.S. Pat. 5,114,611. The use of manganese with various complex ligands to enhance bleaching is also reported in the following United States Patents: 4,728,455; 5,284,944; 5,246,612; 5,256,779; 5,280,117; 5,274,147; 5,153,161; 5,227,084.

The other essential component of the invention is a perfume composition comprising aroma chemicals selected from primary and secondary alcohols, aliphatic aldehydes, hydrocinnamic

aldehydes, esters excluding salicylates, unsaturated ketones and mixtures thereof.

Primary alcohols suitable for the purpose of the invention are 3,7-dimethyl-6-octen-1-ol, 3,7-dimethyl-2,6-octadien-1-ol, phenyl ethyl alcohol, 1-pentanol, 3-methyl-5-phenyl and cyclohexyl ethyl alcohol. Preferred primary alcohols are 3,7-dimethyl-6-octen-1-ol, 3,7-dimethyl-2,6-octadien-1-ol and phenyl ethyl alcohol.

Secondary alcohols suitable for use in the perfume composition are cyclohexanol, 2-tertiary butyl, 4-methyl-3-decen-5-ol, cyclohexanol, 4-tertiary butyl and 4-iso propyl cyclohexanol. Preferred secondary alcohols are cyclohexanol, 2-tertiary butyl and 4-methyl-3-decen-5-ol. When used such alcohols compounds will be at a level of from 1% to 50%, preferably at a level of from 20% to 45% and more preferably from 25% to 35% by weight of the perfume composition.

Aliphatic aldehydes suitable for the purpose of the invention are octanal, nonanal, decanal, undecanal, dodecanal, 10-undecenal, 2-methyl undecanal and 2-methyl decanal.

Hydrocinnamic aldehydes suitable for the purpose of the invention are 2-methyl-3-(4-tertiary butyl phenyl) propanal and 2-methyl-3-(4-iso propyl phenyl) propanal. When used such aliphatic and hydrocinnamic aldehydes will be at a level of up to 30%, preferably at a level of up to 20% and more preferably up to 10% by weight of the perfume composition.

Esters, excluding salicylates, suitable for the purpose of the invention are benzyl acetate, benzyl propionate, phenyl ethyl acetate, citronellyl acetate, geranyl acetate, 2-methyl-3-phenyl-propan-2-yl acetate, 4-tertiary butyl cyclohexyl acetate, 2-tertiary butyl cyclohexyl acetate, hexahydro-4,7-methano-inden-5-yl acetate, hexahydro-4,7-methano-inden-6-yl acetate, hexahydro-4,7-methano-inden-5-yl propionate, hexahydro-4,7-methano-inden-6-yl propionate and methyl benzoate. Preferred esters, excluding salicylates, are 2-methyl-3-phenyl-propan-2-yl acetate, 2-tertiary butyl cyclohexyl acetate, hexahydro-4,7-methano-inden-5-yl acetate, hexahydro-4,7-methano-inden-6-yl acetate, hexahydro-4,7-methano-inden-5-yl propionate, hexahydro-4,7-

methano-inden-6-yl propionate and methyl benzoate. When used such esters excluding salicylates will be at a level of from 5% to 50%, preferably at a level of from 10% to 40% and more preferably from 25% to 35% by weight of the perfume composition.

Unsaturated ketones suitable for the purpose of the invention are 7-acetyl 1,2,3,4,5,6,7,8-octanhydro 1,1,6,7 tetra methyl naphthalene, 3-buten-2-one 3-methyl-4-(2,6,6, trimethyl-2-cyclohexen-1-yl), 3-buten-2-one 4-(2,6,6-trimethyl-1-cyclohexen-1-yl), 3-buten-2-one 4-(2,6,6-trimethyl-2-cyclohexen-1-yl) and ketone cedr-8-enyl methyl. When used such unsaturated ketones will be at a level of from up to 30%, preferably at a level of up to 25% by weight of the perfume composition.

The total sum of the weight of said aroma chemicals, described herein before, present in the perfume composition is at least 30%, preferably at least 50% and more preferably at least 80% by weight of the perfume.

The perfume composition is incorporated in the bleaching composition of the invention at a level of from 0.05% to 2% by weight, preferably from 0.01% to 1% of the bleaching composition.

The incorporation of other ingredients additional to the bleaching system and perfume can be advantageous in enhancing the stability of the perfume. In particular, the bleaching composition may comprise one or more iron and/or manganese chelating agents which further enhances the storage stability of the perfume.

Chelating Agents - Such chelating agents can be selected from the group consisting of amino carboxylates, amino phosphonates, polyfunctionally-substituted aromatic chelating agents and mixtures therein, all as hereinafter defined. Without intending to be bound by theory, it is believed that the benefit of these materials is due in part to their exceptional ability to remove iron and manganese ions from washing solutions by formation of soluble chelates.

Amino carboxylates useful as optional chelating agents include ethylenediaminetetracetates, N-hydroxyethylethylenediaminetriacetates, nitrilotriacetates, ethylenediamine tetrapropionates, triethylenetetraamine-hexacetates, diethylenetriaminepentaacetates, and ethanoldi-glycines, alkali metal, ammonium, and substituted ammonium salts therein and mixtures therein.

Preferred biodegradable non-phosphorus chelants for use herein are ethylenediamine disuccinate ("EDDS"), especially the [S,S] isomer as described in U.S. Patent 4,704,233, ethylenediamine-N,N'-diglutamate (EDDG) and 2-hydroxypropylene-diamine-N,N'-disuccinate (HPDDS) compounds.

Amino phosphonates are also suitable for use as chelating agents in the compositions of the invention when at least low levels of total phosphorus are permitted in detergent compositions, and include ethylenediaminetetrakis (methylenephosphonates) available under the trademark DEQUEST from Monsanto. Preferably, these amino phosphonates do not contain alkyl or alkenyl groups with more than 6 carbon atoms.

Polyfunctionally-substituted aromatic chelating agents are also useful in the compositions herein. See U.S. Patent 3,812,044. Preferred compounds of this type in acid form are dihydroxydisulfobenzenes such as 1,2-dihydroxy-3,5-disulfobenzene.

If utilized, these chelating agents will generally comprise from 0.1% to 10% by weight of the bleaching compositions herein. More preferably, if utilized, the chelating agents will comprise from 0.1% to 3.0% by weight of such compositions.

Additional detergent components

The bleaching compositions of the invention may also contain additional detergent components. The precise nature of these additional components and levels of incorporation thereof will depend on the physical form of the composition, and the nature of the cleaning operation for which it is to be used.

The compositions of the invention may, for example, be formulated as hand and machine laundry detergent compositions, including laundry additive compositions and compositions suitable for use in the pretreatment of stained fabrics and machine dishwashing compositions.

When incorporated in compositions suitable for use in a machine washing method, eg: machine laundry and machine dishwashing methods, the compositions of the invention preferably contain one or more additional deterative components.

For the purpose of the invention, when said bleaching composition comprises additional detergent components, as described herein after, the terms 'bleaching composition' and 'detergent composition' will be used herein after as synonymous.

Deterative Surfactants - Nonlimiting examples of surfactants useful herein typically at levels from 1% to 55%, by weight, include the conventional C₁₁-C₁₈ alkyl benzene sulfonates ("LAS") and primary, branched-chain and random C₁₀-C₂₀ alkyl sulfates ("AS"), the C₁₀-C₁₈ secondary (2,3) alkyl sulfates of the formula $\text{CH}_3(\text{CH}_2)_x(\text{CHOSO}_3^-\text{M}^+)\text{CH}_3$ and $\text{CH}_3(\text{CH}_2)_y(\text{CHOSO}_3^-\text{M}^+)\text{CH}_2\text{CH}_3$ where x and (y + 1) are integers of at least 7, preferably at least 9, and M is a water-solubilizing cation, especially sodium, unsaturated sulfates such as oleyl sulfate, the C₁₀-C₁₈ alkyl alkoxy sulfates ("AE_xS"; especially EO 1-7 ethoxy sulfates), C₁₀-C₁₈ alkyl alkoxy carboxylates (especially the EO 1-5 ethoxycarboxylates), the C₁₀-18 glycerol ethers, the C₁₀-C₁₈ alkyl polyglycosides and their corresponding sulfated polyglycosides, and C₁₂-C₁₈ alpha-sulfonated fatty acid esters. If desired, the conventional nonionic and amphoteric surfactants such as the C₁₂-C₁₈ alkyl ethoxylates ("AE") including the so-called narrow peaked alkyl ethoxylates and C₆-C₁₂ alkyl phenol alkoxyates (especially ethoxylates and mixed ethoxy/propoxy), C₁₂-C₁₈ betaines and sulfobetaines ("sultaines"), C₁₀-C₁₈ amine oxides, and the like, can also be included in the overall compositions. The C₁₀-C₁₈ N-alkyl polyhydroxy fatty acid amides can also be used. Typical

examples include the C₁₂-C₁₈ N-methylglucamides. See WO 9,206,154. Other sugar-derived surfactants include the N-alkoxy polyhydroxy fatty acid amides, such as C₁₀-C₁₈ N (3-methoxypropyl) glucamide. The N-propyl through N-hexyl C₁₂-C₁₈ glucamides can be used for low sudsing. C₁₀-C₂₀ conventional soaps may also be used. If high sudsing is desired, the branched-chain C₁₀-C₁₆ soaps may be used. Mixtures of anionic and nonionic surfactants are especially useful. Other conventional useful surfactants are listed in standard texts.

Adjunct Ingredients

The compositions herein can optionally include one or more other detergent adjunct materials or other materials for assisting or enhancing cleaning performance, treatment of the substrate to be cleaned, or to modify the aesthetics of the detergent composition (e.g., colorants, dyes, etc.). The following are illustrative examples of such adjunct materials.

Builders - Detergent builders can optionally be included in the compositions herein to assist in controlling mineral hardness. Inorganic as well as organic builders can be used. Builders are typically used in fabric laundering compositions to assist in the removal of particulate soils.

The level of builder can vary widely depending upon the end use of the composition and its desired physical form. When present, the compositions will typically comprise at least 1% builder. Granular formulations typically comprise from 10% to 80%, more typically from 15% to 50% by weight, of the detergent builder. Lower or higher levels of builder, however, are not meant to be excluded.

Inorganic or phosphate-containing detergent builders include, but are not limited to, the alkali metal, ammonium and alkanolammonium salts of polyphosphates (exemplified by the tripolyphosphates, pyrophosphates, and glassy polymeric metaphosphates).

Non-phosphate builders may also be used. These can include, but are not restricted to phytic acid, silicates, alkali metal carbonates (including bicarbonates and sesquicarbonates), sulphates,

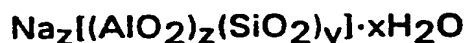
aluminosilicates, monomeric polycarboxylates, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, organic phosphonates and aminoalkylene poly (alkylene phosphonates).

The compositions herein also function in the presence of the so-called "weak" builders (as compared with phosphates) such as citrate, or in the so-called "underbuilt" situation that may occur with zeolite or layered silicate builders.

Examples of silicate builders are the so called 'amorphous' alkali metal silicates, particularly those having a $\text{SiO}_2\text{:Na}_2\text{O}$ ratio in the range 1.6:1 to 3.2:1 and crystalline layered silicates, such as the layered sodium silicates described in U.S. Patent 4,664,839. NaSKS-6 is the trademark for a crystalline layered silicate marketed by Hoechst (commonly abbreviated herein as "SKS-6"). Unlike zeolite builders, the Na SKS-6 silicate builder does not contain aluminum. NaSKS-6 has the delta- $\text{Na}_2\text{Si}_2\text{O}_5$ morphology form of layered silicate. It can be prepared by methods such as those described in German DE-A-3,417,649 and DE-A-3,742,043. SKS-6 is a highly preferred layered silicate for use herein, but other such layered silicates, such as those having the general formula $\text{NaMSi}_x\text{O}_{2x} + 1 \cdot y\text{H}_2\text{O}$ wherein M is sodium or hydrogen, x is a number from 1.9 to 4, preferably 2, and y is a number from 0 to 20, preferably 0 can be used herein. Various other layered silicates from Hoechst include NaSKS-5, NaSKS-7 and NaSKS-11, as the alpha, beta and gamma forms. As noted above, the delta- $\text{Na}_2\text{Si}_2\text{O}_5$ (NaSKS-6 form) is most preferred for use herein. Other silicates may also be useful such as for example magnesium silicate, which can serve as a crispening agent in granular formulations, as a stabilising agent for oxygen bleaches, and as a component of suds control systems.

Examples of carbonate builders are the alkaline earth and alkali metal carbonates as disclosed in German Patent Application No. 2,321,001 published on November 15, 1973.

Aluminosilicate builders are useful in the present invention. Aluminosilicate builders are of great importance in most currently marketed heavy duty granular detergent compositions, and can also be a significant builder ingredient in liquid detergent formulations. Aluminosilicate builders include those having the empirical formula:



wherein z and y are integers of at least 6, the molar ratio of z to y is in the range from 1.0 to 0.5, and x is an integer from 15 to 264.

Useful aluminosilicate ion exchange materials are commercially available. These aluminosilicates can be crystalline or amorphous in structure and can be naturally-occurring aluminosilicates or synthetically derived. A method for producing aluminosilicate ion exchange materials is disclosed in U.S. Patent 3,985,669. Preferred synthetic crystalline aluminosilicate ion exchange materials useful herein are available under the designations Zeolite A, Zeolite P (B), Zeolite MAP and Zeolite X. In an especially preferred embodiment, the crystalline aluminosilicate ion exchange material has the formula:



wherein x is from 20 to 30, especially 27. This material is known as Zeolite A. Dehydrated zeolites ($x = 0 - 10$) may also be used herein. Preferably, the aluminosilicate has a particle size of 0.1-10 microns in diameter.

Organic detergent builders suitable for the purposes of the present invention include, but are not restricted to, a wide variety of polycarboxylate compounds. As used herein, "polycarboxylate" refers to compounds having a plurality of carboxylate groups, preferably at least 3 carboxylates. Polycarboxylate builder can generally be added to the composition in acid form, but can also be added in the form of a neutralised salt. When utilized in salt form, alkali metals, such as sodium, potassium, and lithium, or alkanolammonium salts are preferred.

Included among the polycarboxylate builders are a variety of categories of useful materials. One important category of

polycarboxylate builders encompasses the ether polycarboxylates, including oxydisuccinate, as disclosed in U.S. Patent 3,128,287 and U.S. Patent 3,635,830. See also "TMS/TDS" builders of U.S. Patent 4,663,071. Suitable ether polycarboxylates also include cyclic compounds, particularly alicyclic compounds, such as those described in U.S. Patents 3,923,679; 3,835,163; 4,158,635; 4,120,874 and 4,102,903.

Other useful detergency builders include the ether hydroxypolycarboxylates, copolymers of maleic anhydride with ethylene or vinyl methyl ether, or acrylic acid, 1, 3, 5-trihydroxy benzene-2, 4, 6-trisulphonic acid, and carboxymethyloxysuccinic acid, the various alkali metal, ammonium and substituted ammonium salts of polyacetic acids such as ethylenediamine tetraacetic acid and nitrilotriacetic acid, as well as polycarboxylates such as mellitic acid, succinic acid, oxydisuccinic acid, polymaleic acid, benzene 1,3,5-tricarboxylic acid, carboxymethyloxysuccinic acid, and soluble salts thereof.

Citrate builders, e.g., citric acid and soluble salts thereof (particularly sodium salt), are polycarboxylate builders of particular importance for heavy duty liquid detergent formulations due to their availability from renewable resources and their biodegradability. Citrates can also be used in granular compositions, especially in combination with zeolite and/or layered silicate builders. Oxydisuccinates are also especially useful in such compositions and combinations.

Also suitable in the compositions containing the present invention are the 3,3-dicarboxy-4-oxa-1,6-hexanedioates and the related compounds disclosed in U.S. Patent 4,566,984. Useful succinic acid builders include the C₅-C₂₀ alkyl and alkenyl succinic acids and salts thereof. A particularly preferred compound of this type is dodecenylsuccinic acid. Specific examples of succinate builders include: laurylsuccinate, myristylsuccinate, palmitylsuccinate, 2-dodecenylsuccinate (preferred), 2-pentadecenylsuccinate, and the like. Laurylsuccinates are the preferred builders of this group, and are described in EP 0,200,263.

Other suitable polycarboxylates are disclosed in U.S. Patent 4,144,226 and in U.S. Patent 3,308,067. See also U.S. Pat. 3,723,322.

Fatty acids, e.g., C₁₂-C₁₈ monocarboxylic acids, can also be incorporated into the compositions alone, or in combination with the aforesaid builders, especially citrate and/or the succinate builders, to provide additional builder activity. Such use of fatty acids will generally result in a diminution of sudsing, which should be taken into account by the formulator.

In situations where phosphorus-based builders can be used, and especially in the formulation of bars used for hand-laundrying operations, the various alkali metal phosphates such as the well-known sodium tripolyphosphates, sodium pyrophosphate and sodium orthophosphate can be used. Phosphonate builders such as ethane-1-hydroxy-1,1-diphosphonate and other known phosphonates (see, for example, U.S. Patents 3,159,581; 3,213,030; 3,422,021; 3,400,148 and 3,422,137) can also be used.

Enzymes - Enzymes can be included in the formulations herein for a wide variety of fabric laundering purposes, including removal of protein-based, carbohydrate-based, or triglyceride-based stains, for example, and for the prevention of fugitive dye transfer, and for fabric restoration. The enzymes to be incorporated include proteases, amylases, lipases, cellulases, and peroxidases, as well as mixtures thereof. Other types of enzymes may also be included. They may be of any suitable origin, such as vegetable, animal, bacterial, fungal and yeast origin. However, their choice is governed by several factors such as pH-activity and/or stability optima, thermostability and stability versus active detergents and builders. In this respect bacterial or fungal enzymes are preferred, such as bacterial amylases and proteases, and fungal cellulases.

Enzymes are normally incorporated at levels sufficient to provide up to 5 mg by weight, more typically 0.01 mg to 3 mg, of active enzyme per gram of the composition. Stated otherwise, the compositions herein will typically comprise from

0.001% to 5%, preferably 0.01%-1% by weight of a commercial enzyme preparation.

Suitable examples of proteases are the subtilisins which are obtained from particular strains of *B. subtilis* and *B. licheniformis*. Another suitable protease is obtained from a strain of *Bacillus*, having maximum activity throughout the pH range of 8-12, developed and sold by Novo Industries A/S under the registered trade name ESPERASE. The preparation of this enzyme and analogous enzymes is described in GB 1,243,784 of Novo. Proteolytic enzymes suitable for removing protein-based stains that are commercially available include those sold under the tradenames ALCALASE and SAVINASE by Novo Industries A/S (Denmark) and MAXATASE by International Bio-Synthetics, Inc. (The Netherlands). Other proteases include Protease A (see EP 130,756) and Protease B (see EP257189).

Amylases include, for example, α -amylases described in GB 1,296,839 (Novo), RAPIDASE, International Bio-Synthetics, Inc. and TERMAMYL, Novo Industries. Fungamyl (Novo) is especially useful.

The cellulases usable in the present invention include both bacterial or fungal cellulase. Preferably, they will have a pH optimum of between 5 and 9.5. Suitable cellulases are disclosed in U.S. Patent 4,435,307, which discloses fungal cellulase produced from *Humicola insolens* and *Humicola* strain DSM1800 or a cellulase 212-producing fungus belonging to the genus *Aeromonas*, and cellulase extracted from the hepatopancreas of a marine mollusk (*Dolabella Auricula Solander*). suitable cellulases are also disclosed in GB-A-2.075.028; GB-A-2.095.275 and DE-OS-2.247.832. ENDO A, CAREZYME both from Novo Industries A/S are especially useful.

Suitable lipase enzymes for detergent usage include those produced by microorganisms of the *Pseudomonas* group, such as *Pseudomonas stutzeri* ATCC 19.154, as disclosed in GB 1,372,034. See also lipases in Japanese Patent Application 53,20487, laid open to public inspection on February 24, 1978. This lipase is available from Amano Pharmaceutical Co. Ltd., Nagoya, Japan, under the trade name Lipase P "Amano,"

hereinafter referred to as "Amano-P." Other commercial lipases include Amano-CES, lipases ex *Chromobacter viscosum*, e.g. *Chromobacter viscosum* var. *lipolyticum* NRRLB 3673, commercially available from Toyo Jozo Co., Tagata, Japan; and further *Chromobacter viscosum* lipases from U.S. Biochemical Corp., U.S.A. and Disoynth Co., The Netherlands, and lipases ex *Pseudomonas gladioli*. The LIPOLASE enzyme derived from *Humicola lanuginosa* and commercially available from Novo (see also EP 341,947) is a preferred lipase for use herein.

Peroxidase enzymes are used in combination with oxygen sources, e.g., percarbonate, perborate, persulfate, hydrogen peroxide, etc. They are used for "solution bleaching," i.e. to prevent transfer of dyes or pigments removed from substrates during wash operations to other substrates in the wash solution. Peroxidase enzymes are known in the art, and include, for example, horseradish peroxidase, ligninase, and haloperoxidase such as chloro- and bromo-peroxidase. Peroxidase-containing detergent compositions are disclosed, for example, in PCT International Application WO 89/099813, published October 19, 1989, by O. Kirk, assigned to Novo Industries A/S.

A wide range of enzyme materials and means for their incorporation into synthetic detergent compositions are also disclosed in U.S. Patent 3,553,139. Enzymes are further disclosed in U.S. Patent 4,101,457 and in U.S. Patent 4,507,219. Enzyme materials useful for liquid detergent formulations, and their incorporation into such formulations, are disclosed in U.S. Patent 4,261,868. Enzymes for use in detergents can be stabilized by various techniques. Enzyme stabilisation techniques are disclosed and exemplified in U.S. Patent 3,600,319 and EP 0 199 405. Enzyme stabilisation systems are also described, for example, in U.S. Patent 3,519,570.

Enzyme Stabilisers - The enzymes employed herein are stabilized by the presence of water-soluble sources of calcium and/or magnesium ions in the finished compositions which provide such ions to the enzymes. (Calcium ions are generally

somewhat more effective than magnesium ions and are preferred herein if only one type of cation is being used.) Additional stability can be provided by the presence of various other art-disclosed stabilisers, especially borate species: see Severson, U.S. 4,537,706. Typical detergents, especially liquids, will comprise from 1 to 30, preferably from 2 to 20, more preferably from 5 to 15, and most preferably from 8 to 12, millimoles of calcium ion per liter of finished composition. This can vary somewhat, depending on the amount of enzyme present and its response to the calcium or magnesium ions. The level of calcium or magnesium ions should be selected so that there is always some minimum level available for the enzyme, after allowing for complexation with builders, fatty acids, etc., in the composition. Any water-soluble calcium or magnesium salt can be used as the source of calcium or magnesium ions, including, but not limited to, calcium chloride, calcium sulfate, calcium malate, calcium maleate, calcium hydroxide, calcium formate, and calcium acetate, and the corresponding magnesium salts. A small amount of calcium ion, generally from 0.05 to 0.4 millimoles per liter, is often also present in the composition due to calcium in the enzyme slurry and formula water. In solid detergent compositions the formulation may include a sufficient quantity of a water-soluble calcium ion source to provide such amounts in the laundry liquor. In the alternative, natural water hardness may suffice.

It is to be understood that the foregoing levels of calcium and/or magnesium ions are sufficient to provide enzyme stability. More calcium and/or magnesium ions can be added to the compositions to provide an additional measure of grease removal performance. Accordingly, as a general proposition the compositions herein will typically comprise from 0.05% to 2% by weight of a water-soluble source of calcium or magnesium ions, or both. The amount can vary, of course, with the amount and type of enzyme employed in the composition.

The compositions herein may also optionally, but preferably, contain various additional stabilizers, especially borate-type stabilizers. Typically, such stabilizers will be used at

levels in the compositions from 0.25% to 10%, preferably from 0.5% to 5%, more preferably from 0.75% to 3%, by weight of boric acid or other borate compound capable of forming boric acid in the composition (calculated on the basis of boric acid). Boric acid is preferred, although other compounds such as boric oxide, borax and other alkali metal borates (e.g., sodium ortho-, meta- and pyroborate, and sodium pentaborate) are suitable. Substituted boric acids (e.g., phenylboronic acid, butane boronic acid, and p-bromo phenylboronic acid) can also be used in place of boric acid.

Clay Soil Removal/Anti-redeposition Agents - The compositions according to the present invention can also optionally contain water-soluble ethoxylated amines having clay soil removal and antiredeposition properties. Granular detergent compositions which contain these compounds typically contain from 0.01% to 10.0% by weight of the water-soluble ethoxylates amines; liquid detergent compositions typically contain 0.01% to 5%.

The most preferred soil release and anti-redeposition agent is ethoxylated tetraethylenepentamine. Exemplary ethoxylated amines are further described in U.S. Patent 4,597,898, VanderMeer, issued July 1, 1986. Another group of preferred clay soil removal-antiredeposition agents are the cationic compounds disclosed in EP 111,965. Other clay soil removal/antiredeposition agents which can be used include the ethoxylated amine polymers disclosed in EP 111,984; the zwitterionic polymers disclosed in EP 112,592; and the amine oxides disclosed in U.S. Patent 4,548,744. Other clay soil removal and/or anti redeposition agents known in the art can also be utilized in the compositions herein. Another type of preferred antiredeposition agent includes the carboxy methyl cellulose (CMC) materials. These materials are well known in the art.

Polymeric Soil Release Agent - Any polymeric soil release agent known to those skilled in the art can optionally be employed in the compositions and processes of this invention. Polymeric soil

release agents are characterized by having both hydrophilic segments, to hydrophilize the surface of hydrophobic fibers, such as polyester and nylon, and hydrophobic segments, to deposit upon hydrophobic fibers and remain adhered thereto through completion of washing and rinsing cycles and, thus, serve as an anchor for the hydrophilic segments. This can enable stains occurring subsequent to treatment with the soil release agent to be more easily cleaned in later washing procedures.

Soil release agents characterized by poly(vinyl ester) hydrophobe segments include graft copolymers of poly(vinyl ester), e.g., C₁-C₆ vinyl esters, preferably poly(vinyl acetate) grafted onto polyalkylene oxide backbones, such as polyethylene oxide backbones (see EP 0 219 048). Commercially available soil release agents of this kind include the SOKALAN type of material, e.g., SOKALAN HP-22, available from BASF (West Germany).

One type of preferred soil release agent is a copolymer having random blocks of ethylene terephthalate and polyethylene oxide (PEO) terephthalate. The molecular weight of this polymeric soil release agent is in the range of from 25,000 to 55,000. See U.S. Patent 3,959,230 to Hays and U.S. Patent 3,893,929.

Another preferred polymeric soil release agent is a polyester with repeat units of ethylene terephthalate units contains 10-15% by weight of ethylene terephthalate units together with 90-80% by weight of polyoxyethylene terephthalate units, derived from a polyoxyethylene glycol of average molecular weight 300-5,000. Examples of this polymer include the commercially available material ZELCON 5126 (from Dupont) and MILEASE T (from ICI). See also U.S. Patent 4,702,857.

Another preferred polymeric soil release agent is a sulfonated product of a substantially linear ester oligomer comprised of an oligomeric ester backbone of terephthaloyl and oxyalkyleneoxy repeat units and terminal moieties covalently attached to the backbone. These soil release agents are described fully in U.S. Patent 4,968,451. Other suitable polymeric soil release agents include the terephthalate polyesters

of U.S. Patent 4,711,730, the anionic end-capped oligomeric esters of U.S. Patent 4,721,580 and the block polyester oligomeric compounds of U.S. Patent 4,702,857.

Preferred polymeric soil release agents also include the soil release agents of U.S. Patent 4,877,896, which discloses anionic, especially sulfoaroyl, end-capped terephthalate esters.

If utilized, soil release agents will generally comprise from 0.01% to 10.0%, by weight, of the compositions herein, typically from 0.1% to 5%, preferably from 0.2% to 3.0%.

Still another preferred soil release agent is an oligomer with repeat units of terephthaloyl units, sulfoisoterephthaloyl units, oxyethyleneoxy and oxy-1,2-propylene units. The repeat units form the backbone of the oligomer and are preferably terminated with modified isethionate end-caps. A particularly preferred soil release agent of this type comprises one sulfoisophthaloyl unit, 5 terephthaloyl units, oxyethyleneoxy and oxy-1,2-propyleneoxy units in a ratio of from 1.7 to 1.8, and two end-cap units of sodium 2-(2-hydroxyethoxy)-ethanesulfonate. Said soil release agent also comprises from 0.5% to 20%, by weight of the oligomer, of a crystalline-reducing stabilizer, preferably selected from xylene sulfonate, cumene sulfonate, toluene sulfonate, and mixtures thereof.

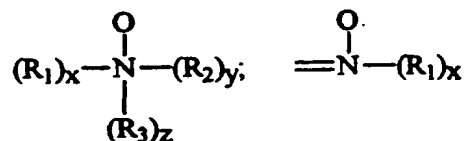
Dye Transfer Inhibiting Agents

The compositions according to the present invention may also include one or more materials effective for inhibiting the transfer of dyes from one fabric to another during the cleaning process. Generally, such dye transfer inhibiting agents include polyvinyl pyrrolidone polymers, polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, manganese phthalocyanine, peroxidases, and mixtures thereof. If used, these agents typically comprise from 0.01% to 10% by weight of the composition, preferably from 0.01% to 5%, and more preferably from 0.05% to 2%.

More specifically, the polyamine N-oxide polymers preferred for use herein contain units having the following structural formula: $R-A_x-P$; wherein P is a polymerizable unit to which an N-

O group can be attached or the N-O group can form part of the polymerizable unit or the N-O group can be attached to both units; A is one of the following structures: -NC(O)-, -C(O)O-, -S-, -O-, -N=; x is 0 or 1; and R is aliphatic, ethoxylated aliphatics, aromatics, heterocyclic or alicyclic groups or any combination thereof to which the nitrogen of the N-O group can be attached or the N-O group is part of these groups. Preferred polyamine N-oxides are those wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine and derivatives thereof.

The N-O group can be represented by the following general structures:



wherein R_1 , R_2 , R_3 are aliphatic, aromatic, heterocyclic or alicyclic groups or combinations thereof; x, y and z are 0 or 1; and the nitrogen of the N-O group can be attached or form part of any of the aforementioned groups. The amine oxide unit of the polyamine N-oxides has a $\text{pK}_a < 10$, preferably $\text{pK}_a < 7$, more preferred $\text{pK}_a < 6$.

Any polymer backbone can be used as long as the amine oxide polymer formed is water-soluble and has dye transfer inhibiting properties. Examples of suitable polymeric backbones are polyvinyls, polyalkylenes, polyesters, polyethers, polyamide, polyimides, polyacrylates and mixtures thereof. These polymers include random or block copolymers where one monomer type is an amine N-oxide and the other monomer type is an N-oxide. The amine N-oxide polymers typically have a ratio of amine to the amine N-oxide of 10:1 to 1:1,000,000. However, the number of amine oxide groups present in the polyamine oxide polymer can be varied by appropriate copolymerization or by an appropriate degree of N-oxidation. The polyamine oxides can be obtained in almost any degree of polymerization. Typically, the average molecular weight is within the range of 500 to 1,000,000; more

preferred 1,000 to 500,000; most preferred 5,000 to 100,000. This preferred class of materials can be referred to as "PVNO".

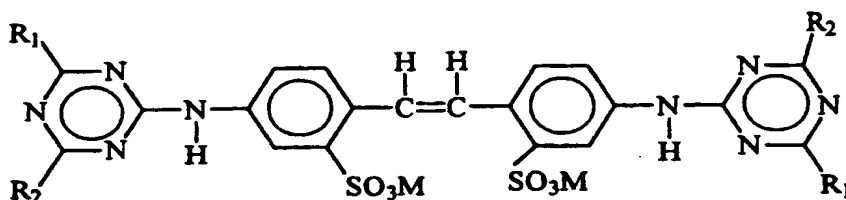
The most preferred polyamine N-oxide useful in the compositions herein is poly(4-vinylpyridine-N-oxide) which as an average molecular weight of 50,000 and an amine to amine N-oxide ratio of 1:4.

Copolymers of N-vinylpyrrolidone and N-vinylimidazole polymers (referred to as a class as "PVPVI") are also preferred for use herein. Preferably the PVPVI has an average molecular weight range from 5,000 to 1,000,000, more preferably from 5,000 to 200,000, and most preferably from 10,000 to 20,000. (The average molecular weight range is determined by light scattering as described in Barth, et al., Chemical Analysis, Vol 113. "Modern Methods of Polymer Characterization".) The PVPVI copolymers typically have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1:1 to 0.2:1, more preferably from 0.8:1 to 0.3:1, most preferably from 0.6:1 to 0.4:1. These copolymers can be either linear or branched.

The present invention compositions also may employ a polyvinylpyrrolidone ("PVP") having an average molecular weight of from 5,000 to 400,000, preferably from 5,000 to 200,000, and more preferably from 5,000 to 50,000. PVP's are known to persons skilled in the detergent field; see, for example, EP-A-262,897 and EP-A-256,696. Compositions containing PVP can also contain polyethylene glycol ("PEG") having an average molecular weight from 500 to 100,000, preferably from 1,000 to 10,000. Preferably, the ratio of PEG to PVP on a ppm basis delivered in wash solutions is from 2:1 to 50:1, and more preferably from 3:1 to 10:1.

The detergent compositions herein may also optionally contain from 0.005% to 5% by weight of certain types of hydrophilic optical brighteners which also provide a dye transfer inhibition action. If used, the compositions herein will preferably comprise from 0.01% to 1% by weight of such optical brighteners.

The hydrophilic optical brighteners useful in the present invention are those having the structural formula:



wherein R_1 is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R_2 is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R_1 is anilino, R_2 is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the compositions herein.

When in the above formula, R_1 is anilino, R_2 is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation.

When in the above formula, R_1 is anilino, R_2 is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Other specific optical brightener species which may be used in the present invention provide especially effective dye transfer inhibition performance benefits when used in combination with the selected polymeric dye transfer inhibiting agents hereinbefore described. The combination of such selected polymeric materials (e.g., PVNO and/or PVPVI) with such selected optical brighteners

(e.g., Tinopal UNPA-GX, Tinopal 5BM-GX and/or Tinopal AMS-GX) provides significantly better dye transfer inhibition in aqueous wash solutions than does either of these two detergent composition components when used alone. Without being bound by theory, it is believed that such brighteners work this way because they have high affinity for fabrics in the wash solution and therefore deposit relatively quick on these fabrics. The extent to which brighteners deposit on fabrics in the wash solution can be defined by a parameter called the "exhaustion coefficient". The exhaustion coefficient is in general as the ratio of a) the brightener material deposited on fabric to b) the initial brightener concentration in the wash liquor. Brighteners with relatively high exhaustion coefficients are the most suitable for inhibiting dye transfer in the context of the present invention.

Of course, it will be appreciated that other, conventional optical brightener types of compounds can optionally be used in the present compositions to provide conventional fabric "brightness" benefits, rather than a true dye transfer inhibiting effect. Such usage is conventional and well-known to detergent formulations.

Conventional optical brighteners or other brightening or whitening agents known in the art can be incorporated at levels typically from 0.05% to 1.2%, by weight, into the detergent compositions herein. Commercial optical brighteners which may be useful in the present invention can be classified into subgroups, which include, but are not necessarily limited to, derivatives of stilbene, pyrazoline, coumarin, carboxylic acid, methinecyanines, dibenzothiophene-5,5-dioxide, azoles, 5- and 6-membered-ring heterocycles, and other miscellaneous agents. Examples of such brighteners are disclosed in "The Production and Application of Fluorescent Brightening Agents", M. Zahradnik, Published by John Wiley & Sons, New York (1982).

Specific examples of optical brighteners which are useful in the present compositions are those identified in U.S. Patent 4,790,856. These brighteners include the PHORWHITE series of brighteners from Verona. Other brighteners disclosed in this

reference include: Tinopal UNPA, Tinopal CBS and Tinopal 5BM; available from Ciba-Geigy; Artic White CC and Artic White CWD, available from Hilton-Davis, located in Italy; the 2-(4-stryl-phenyl)-2H-naphthol[1,2-d]triazoles; 4,4'-bis- (1,2,3-triazol-2-yl)-stil- benes; 4,4'-bis(stryl)bisphenyls; and the aminocoumarins. Specific examples of these brighteners include 4-methyl-7-diethyl- amino coumarin; 1,2-bis(-venzimidazol-2-yl)ethylene; 1,3-diphenyl-phrazolines; 2,5-bis(benzoxazol-2-yl)thiophene; 2-stryl-naph-[1,2-d]oxazole; and 2-(stilbene-4-yl)-2H-naphtho- [1,2-d]triazole. See also U.S. Patent 3,646,015. Anionic brighteners are preferred herein.

Suds Suppressors - Compounds for reducing or suppressing the formation of suds can be incorporated into the compositions of the present invention. Suds suppression can be of particular importance in the so-called "high concentration cleaning process" and in front-loading European-style washing machines.

A wide variety of materials may be used as suds suppressors, and suds suppressors are well known to those skilled in the art. See, for example, Kirk Othmer Encyclopedia of Chemical Technology, Third Edition, Volume 7, pages 430-447 (John Wiley & Sons, Inc., 1979). One category of suds suppressor of particular interest encompasses monocarboxylic fatty acid and soluble salts therein. See U.S. Patent 2,954,347. The monocarboxylic fatty acids and salts thereof used as suds suppressor typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts.

The bleaching compositions herein may also contain non-surfactant suds suppressors. These include, for example: high molecular weight hydrocarbons such as paraffin, fatty acid esters (e.g., fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C₁₈-C₄₀ ketones (e.g., stearone), etc. Other suds inhibitors include N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra-alkyldiamine chlortriazines formed as products of cyanuric chloride with two or three moles

of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, and monostearyl phosphates such as monostearyl alcohol phosphate ester and monostearyl di-alkali metal (e.g., K, Na, and Li) phosphates and phosphate esters. The hydrocarbons such as paraffin and haloparaffin can be utilized in liquid form. The liquid hydrocarbons will be liquid at room temperature and atmospheric pressure, and will have a pour point in the range of -40°C and 50°C , and a minimum boiling point not less than 110°C (atmospheric pressure). It is also known to utilize waxy hydrocarbons, preferably having a melting point below 100°C . The hydrocarbons constitute a preferred category of suds suppressor for detergent compositions. Hydrocarbon suds suppressors are described, for example, in U.S. Patent 4,265,779. The hydrocarbons, thus, include aliphatic, alicyclic, aromatic, and heterocyclic saturated or unsaturated hydrocarbons having from 12 to 70 carbon atoms. The term "paraffin," as used in this suds suppressor discussion, is intended to include mixtures of true paraffins and cyclic hydrocarbons.

Another preferred category of non-surfactant suds suppressors comprises silicone suds suppressors. This category includes the use of polyorganosiloxane oils, such as polydimethylsiloxane, dispersions or emulsions of polyorganosiloxane oils or resins, and combinations of polyorganosiloxane with silica particles wherein the polyorganosiloxane is chemisorbed or fused onto the silica. Silicone suds suppressors are well known in the art and are, for example, disclosed in U.S. Patent 4,265,779 and EP 354016.

Other silicone suds suppressors are disclosed in U.S. Patent 3,455,839 which relates to compositions and processes for defoaming aqueous solutions by incorporating therein small amounts of polydimethylsiloxane fluids.

Mixtures of silicone and silanated silica are described, for instance, in German Patent Application DOS 2,124,526. Silicone defoamers and suds controlling agents in granular detergent compositions are disclosed in U.S. Patent 3,933,672 and in U.S. Patent 4,652,392.

An exemplary silicone based suds suppressor for use herein is a suds suppressing amount of a suds controlling agent consisting essentially of:

- (i) polydimethylsiloxane fluid having a viscosity of from 20 cs. to 1,500 cs. at 25°C;
- (ii) from 5 to 50 parts per 100 parts by weight of (i) of siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units of SiO_2 units in a ratio of from $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and to SiO_2 units of from 0.6:1 to 1.2:1; and
- (iii) from 1 to 20 parts per 100 parts by weight of (i) of a solid silica gel.

In the preferred silicone suds suppressor used herein, the solvent for a continuous phase is made up of certain polyethylene glycols or polyethylene-polypropylene glycol copolymers or mixtures thereof (preferred), or polypropylene glycol. The primary silicone suds suppressor is branched/crosslinked and preferably not linear.

To illustrate this point further, typical liquid laundry detergent compositions with controlled suds will optionally comprise from 0.001 to 1, preferably from 0.01 to 0.7, most preferably from 0.05 to 0.5, weight % of said silicone suds suppressor, which comprises (1) a nonaqueous emulsion of a primary antifoam agent which is a mixture of (a) a polyorganosiloxane, (b) a resinous siloxane or a silicone resin-producing silicone compound, (c) a finely divided filler material, and (d) a catalyst to promote the reaction of mixture components (a), (b) and (c), to form silanolates; (2) at least one nonionic silicone surfactant; and (3) polyethylene glycol or a copolymer of polyethylene-polypropylene glycol having a solubility in water at room temperature of more than 2 weight %; and without polypropylene glycol. Similar amounts can be used in granular compositions, gels, etc. See also U.S. Patents 4,978,471 and 4,983,316; 5,288,431 and U.S. Patents 4,639,489 and 4,749,740, Aizawa et al at column 1, line 46 through column 4, line 35.

The silicone suds suppressor herein preferably comprises polyethylene glycol and a copolymer of polyethylene

glycol/polypropylene glycol, all having an average molecular weight of less than 1,000, preferably between 100 and 800. The polyethylene glycol and polyethylene/polypropylene copolymers herein have a solubility in water at room temperature of more than 2 weight %, preferably more than 5 weight %.

The preferred solvent herein is polyethylene glycol having an average molecular weight of less than 1,000, more preferably between 100 and 800, most preferably between 200 and 400, and a copolymer of polyethylene glycol/polypropylene glycol, preferably PPG 200/PEG 300. Preferred is a weight ratio of between 1:1 and 1:10, most preferably between 1:3 and 1:6, of polyethylene glycol:copolymer of polyethylene-polypropylene glycol.

The preferred silicone suds suppressors used herein do not contain polypropylene glycol, particularly of 4,000 molecular weight. They also preferably do not contain block copolymers of ethylene oxide and propylene oxide, like PLURONIC L101.

Other suds suppressors useful herein comprise the secondary alcohols (e.g., 2-alkyl alkanols) and mixtures of such alcohols with silicone oils, such as the silicones disclosed in U.S. 4,798,679, 4,075,118 and EP 150,872. The secondary alcohols include the C₆-C₁₆ alkyl alcohols having a C₁-C₁₆ chain. A preferred alcohol is 2-butyl octanol, which is available from Condea under the trademark ISOFOL 12. Mixtures of secondary alcohols are available under the trademark ISALCHEM 123 from Enichem. Mixed suds suppressors typically comprise mixtures of alcohol + silicone at a weight ratio of 1:5 to 5:1.

For any detergent compositions to be used in automatic laundry washing machines, suds should not form to the extent that they overflow the washing machine. Suds suppressors, when utilized, are preferably present in a "suds suppressing amount." By "suds suppressing amount" is meant that the formulator of the composition can select an amount of this suds controlling agent that will sufficiently control the suds to result in a low-sudsing laundry detergent for use in automatic laundry washing machines.

The compositions herein will generally comprise from 0% to 5% of suds suppressor. When utilized as suds suppressors, monocarboxylic fatty acids, and salts therein, will be present typically in amounts up to 5%, by weight, of the detergent composition. Preferably, from 0.5% to 3% of fatty monocarboxylate suds suppressor is utilized. Silicone suds suppressors are typically utilized in amounts up to 2.0%, by weight, of the detergent composition, although higher amounts may be used. This upper limit is practical in nature, due primarily to concern with keeping costs minimized and effectiveness of lower amounts for effectively controlling sudsing. Preferably from 0.01% to 1% of silicone suds suppressor is used, more preferably from 0.25% to 0.5%. As used herein, these weight percentage values include any silica that may be utilized in combination with polyorganosiloxane, as well as any adjunct materials that may be utilized. Monostearyl phosphate suds suppressors are generally utilized in amounts ranging from 0.1% to 2%, by weight, of the composition. Hydrocarbon suds suppressors are typically utilized in amounts ranging from 0.01% to 5.0%, although higher levels can be used. The alcohol suds suppressors are typically used at 0.2%-3% by weight of the finished compositions.

Fabric Softeners - Various through-the-wash fabric softeners, especially the impalpable smectite clays of U.S. Patent 4,062,647, as well as other softener clays known in the art, can optionally be used typically at levels of from 0.5% to 10% by weight in the present compositions to provide fabric softener benefits concurrently with fabric cleaning. Clay softeners can be used in combination with amine and cationic softeners as disclosed, for example, in U.S. Patent 4,375,416 and U.S. Patent 4,291,071.

Other Ingredients - A wide variety of other functional ingredients useful in detergent compositions can be included in the compositions herein, including other active ingredients, carriers, hydrotropes, processing aids, dyes or pigments, solvents for

liquid formulations, solid fillers for bar compositions, etc. If high sudsing is desired, suds boosters such as the C₁₀-C₁₆ alkanolamides can be incorporated into the compositions, typically at 1%-10% levels. The C₁₀-C₁₄ monoethanol and diethanol amides illustrate a typical class of such suds boosters. Use of such suds boosters with high sudsing adjunct surfactants such as the amine oxides, betaines and sultaines noted above is also advantageous. If desired, soluble magnesium salts such as MgCl₂, MgSO₄, and the like, can be added at levels of, typically, 0.1%-2%, to provide additional suds and to enhance grease removal performance.

Various deterative ingredients employed in the present compositions optionally can be further stabilized by absorbing said ingredients onto a porous hydrophobic substrate, then coating said substrate with a hydrophobic coating. Preferably, the deterative ingredient is admixed with a surfactant before being absorbed into the porous substrate. In use, the deterative ingredient is released from the substrate into the aqueous washing liquor, where it performs its intended deterative function.

To illustrate this technique in more detail, a porous hydrophobic silica (trademark SIPERNAT D10, DeGussa) is admixed with a proteolytic enzyme solution containing 3%-5% of C₁₃-15 ethoxylated alcohol (EO 7) nonionic surfactant. Typically, the enzyme/surfactant solution is 2.5 X the weight of silica. The resulting powder is dispersed with stirring in silicone oil (various silicone oil viscosities in the range of 500-12,500 can be used). The resulting silicone oil dispersion is emulsified or otherwise added to the final detergent matrix. By this means, ingredients such as the aforementioned enzymes, bleaches, bleach activators, bleach catalysts, photoactivators, dyes, fluorescers, fabric conditioners and hydrolyzable surfactants can be "protected" for use in detergents.

The detergent compositions herein will preferably be formulated such that, during use in aqueous cleaning operations, the wash water will have a pH of between 6.5 and 11, preferably between 7.5 and 10.5. Laundry products are typically at pH 9-11. Techniques for controlling pH at recommended usage

levels include the use of buffers, alkalis, acids, etc., and are well known to those skilled in the art.

The bulk density of granular bleaching compositions (so-called granular detergent compositions) is typically at least 450 g/litre, more usually at least 600 g/litre and more preferably from 650 g/litre to 1000 g/litre.

The invention is illustrated in the following non limiting examples, in which all percentages are on a weight basis unless otherwise stated.

In the bleaching compositions of the invention, the abbreviated component identifications have the following meanings:

| | | |
|------------------------------|---|---|
| LAS | : | Sodium linear C ₁₂ alkyl benzene sulphonate |
| TAS | : | Sodium tallow alkyl sulphate |
| XYAS | : | Sodium C _{1X} - C _{1Y} alkyl sulphate |
| 25EY | : | A C ₁₂₋₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide |
| 45EY | : | A C ₁₄ - C ₁₅ predominantly linear primary alcohol condensed with an average of Y moles of ethylene oxide |
| XYEZX | : | C _{1X} - C _{1Y} sodium alkyl sulphate condensed with an average of Z moles of ethylene oxide per mole |
| polyhydroxy fatty acid amide | : | N-Lauroyl N-Methyl Glucamine |
| TFAA | : | C ₁₆ -C ₁₈ alkyl N-methyl glucamide. |

| | | |
|--------------|---|--|
| NaSKS-6 | : | Crystalline layered silicate of formula δ - $\text{Na}_2\text{Si}_2\text{O}_5$ |
| Carbonate | : | Anhydrous sodium carbonate |
| Silicate | : | Amorphous sodium silicate ($\text{SiO}_2:\text{Na}_2\text{O}$ ratio normally follows) |
| MA/AA | : | Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 80,000 |
| Zeolite A | : | Hydrated Sodium Aluminosilicate of formula $\text{Na}_{12}(\text{AlO}_2\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$ having a primary particle size in the range from 1 to 10 micrometers |
| Photobleach | : | Tetra sulphonated zinc phthalocyanine |
| Citrate | : | Tri-sodium citrate dihydrate |
| Citric acid | : | Anhydrous Citric Acid |
| PB1 | : | Sodium perborate monohydrate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2$ |
| PB4 | : | Sodium perborate tetrahydrate bleach of nominal formula $\text{NaBO}_2 \cdot \text{H}_2\text{O}_2 \cdot 3\text{H}_2\text{O}$ |
| Percarbonate | : | Anhydrous sodium percarbonate bleach of empirical formula $2\text{Na}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}_2$ coated with a mixed salt of formula $\text{Na}_2\text{SO}_4 \cdot n \cdot \text{Na}_2\text{CO}_3$ where n is 0.29 and where the weight ratio of percarbonate to mixed salt is 39:1 |
| TAED | : | Tetraacetyl ethylene diamine |
| Savinase | : | Proteolytic enzyme activity 4 KNPU/g |
| Lipolase | : | Lipolytic enzyme activity 100 KLU/g |

| | | |
|---------------------------------|---|--|
| Cellulase | : | Cellulosic enzyme activity of 1000 CEVU/g |
| Endo A | : | Cellulytic enzyme activity 5000 SCEVU/g |
| Termamyl 60T | : | Amylolytic enzyme activity of 300 KNU/g |
| all sold by NOVO Industries A/S | | |
| PVNO | : | Polyvinyl pyridine N-oxide polymer of molecular weight 10,000 |
| MgSO ₄ | : | Anhydrous Magnesium Sulphate |
| SRP | : | modified anionic polyester Soil Release Polymer |
| CMC | : | Sodium carboxymethyl cellulose |
| EDDS | : | Ethylenediamine -N, N'- disuccinic acid, [S,S] isomer in the form of the sodium salt. |
| Brightener | : | Disodium 4,4'-bis-(2-sulphostyryl)-biphenyl. |
| DETPMP | : | Diethylenetriamine penta (Methylene phosphonic acid) marketed by Monsanto under the Trade name Dequest 2060. |
| Mixed Suds suppressor | : | 25% paraffin wax Mpt 50°C, 17% hydrophobic silica, 58% paraffin oil. |

Example 1

The following perfume formulations were prepared

| Perfume 1 | % |
|-------------------------|----|
| Hexyl cinnamic aldehyde | 10 |
| Hexyl salicylate | 20 |

| | |
|--|----|
| Phenyl ethyl alcohol | 20 |
| Citronellol | 12 |
| Geraniol | 8 |
| 2-Methyl-3-(4-tertiary butyl phenyl) propanal | 10 |
| Phenyl ethyl acetate | 2 |
| Benzyl acetate | 5 |
| 4-tertiary butyl cyclohexyl acetate | 5 |
| 3-Buten-2-one, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl) | 3 |
| 10-undecenal (10% in DPG) | 5 |

| | |
|---|----------|
| Perfume 2 | % |
| Benzyl salicylate | 5 |
| Hexyl salicylate | 10 |
| Phenyl ethyl alcohol | 15 |
| 4-Iso propyl cyclohexanol | 5 |
| Citronellol | 10 |
| 3-Buten-2-one, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl) | 15 |
| Heliotropine | 4 |
| 7-Acetyl, 1, 2, 3, 4, 5, 6, 7, 8-octahydro 1, 1, 6, 7 tetra methyl naphtalene | 5 |
| Benzyl acetate | 7 |
| 4-tertiary butyl cyclohexyl acetate | 20 |
| 2-Methyl-3-phenyl propan-2-yl acetate | 4 |

Storage stability of said perfume compositions in term of grade stability

Method for measuring the perfume grade stability

Perfume samples are at least 24 hours old. The samples are coded to preserve anonymity and the results are recorded on

individual sheets. The panel is held in an odour-free room. The detergent is poured into a clean plastic cup and covered immediately with a plastic lid. 1 % solutions are then made by adding hot water (50°C) to a beaker along with the product. This is covered immediately with a watch glass.

Panel odour grading is carried out by a minimum of three expert judges. In this instance, expert is defined as a person having at least 6 months training with demonstrated evidence of olfactive sensitivity. All grades for this work were given versus a laboratory prepared standard product (grade 10.0) on a 1-10 scale. The individual grades are only averaged when the highest and lowest grades do not differ by more than 2 panel grades. Where differences are greater, that product is repanelled as soon as possible on a subsequent panel.

For each perfume formulations sprayed onto the bleaching composition at least 1 stability grade enhancement was recorded.

Example 2

The following perfumed bleaching compositions were prepared (parts by weight). Compositions A, B, C, D are in accordance with the present invention, wherein the perfume is selected from one of those defined in Example 1 and sprayed onto the finished detergent product.

| | A | B | C | D |
|--------------------|------|------|-----|------|
| LAS | - | - | - | 6.92 |
| TAS | - | - | - | 2.05 |
| 45AS/25AS (3:1) | - | - | 9.1 | - |
| 45AS | 6.86 | 6.86 | - | - |
| 35AE3S | | | 2.3 | |

| | | | | |
|---------------------------------|------|------|------|-------|
| C25E3S | 1.71 | 1.71 | - | 0.16 |
| C45E7 | - | - | - | 4.0 |
| C25E5 | 2.21 | 2.21 | - | - |
| C24E5 | | | 4.5 | |
| C25E3 | 1.16 | 1.16 | - | - |
| polyhydroxy fatty acid amide | 1.45 | 1.45 | - | - |
| TFAA | - | - | 2.0 | |
| Zeolite A | 10.2 | 10.2 | 10.2 | 20.2 |
| Citrate | - | - | - | 5.5 |
| Citric | 2.5 | 2.3 | - | - |
| SKS-6 | 9.2 | 8.5 | - | - |
| Na SKS-6/citric acid (79:21) | - | - | 10.6 | - |
| Carbonate | 5.8 | 9.8 | 7.6 | 15.4 |
| Silicate (2.0 ratio) | - | - | 0.15 | 3.0 |
| Bicarbonate | - | - | 0.28 | - |
| Sulphate | - | 8.0 | 0.27 | - |
| MA/AA | 3.85 | 3.0 | 3.1 | 4.0 |
| CMC | 0.30 | 0.30 | 0.4 | 0.31 |
| SRP | 0.20 | 0.15 | 0.20 | 0.30 |
| PVPVI | - | - | - | 0.01 |
| PVNO | 0.02 | - | 0.03 | 0.01 |
| Savinase | 0.41 | 0.25 | 0.55 | 1.4 |
| Lipolase | 0.11 | 0.07 | 0.15 | 0.36 |
| Cellulase | 0.12 | - | 0.28 | - |
| Endo A | 0.08 | 0.12 | - | 0.13 |
| Termamyl 60T | - | - | 0.27 | - |
| PB4 | - | - | - | 11.64 |
| PB1 | - | - | - | 8.7 |
| TAED | 4.7 | 1.6 | 5.0 | 5.0 |
| DETPMP | - | - | 0.5 | 0.38 |
| MgSO4 | 0.38 | 0.38 | 0.38 | 0.40 |
| Percarbonate | 16.9 | 10.0 | 22.5 | - |
| EDDS | 0.21 | 0.21 | - | - |

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| | | | | |
|-----------------------|--------|--------|--------|--------|
| Brightener | 0.22 | 0.18 | 0.22 | 0.19 |
| Photoactivated bleach | 0.002 | 0.002 | 0.002 | 0.002 |
| Suds suppressor | 2.75 | 2.75 | 1.5 | 0.85 |
| perfumes | 0.3(1) | 0.3(2) | 0.3(1) | 0.3(2) |

Water minors and miscellaneous to balance

(1) perfume formulation 1

(2) perfume formulation 2

The compositions in accordance with the invention were all seen having an enhanced perfume stability of at least 1 grade.

WHAT IS CLAIMED IS:

1-A perfumed bleaching composition containing:

a-a bleaching system selected from

i)-a perhydrate in amount of from 0.1 % to 60% by weight and combined with a bleach activator in amount of from 0.1 % to 60% by weight,

ii)-a preformed peracid in amount of from 0.1 % to 60% by weight,

and any mixtures thereof,

wherein said perhydrate and/or said preformed peracid are coated; and

b-a perfume in amount from 0.05% to 2% by weight which comprises aroma chemicals selected from: primary and secondary alcohols, aliphatic aldehydes, hydrocinnamic aldehydes, esters excluding salicylates, unsaturated ketones and mixtures thereof, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 30% by weight of the perfume.

2-A perfumed bleaching composition according to Claim 1, wherein said perhydrate and/or said preformed peracid is provided with a coating material which prevents H₂O₂ and/or perhydroxide anion from diffusion such that less than 5% by weight of said perhydroxide source is diffused upon storage.

3-A perfumed bleaching composition according to either one of Claim 1 or 2, wherein said bleach activator contains one or more N- or O-acyl groups.

4-A perfumed bleaching composition according to any one of Claims 1-3, wherein said perhydrate and/or said preformed peracid is provided with a coating material selected from citrate, sodium silicate, borate, surfactant and mixture of alkali metal sulphate and carbonate.

5- A perfumed bleaching composition according to any one of Claims 1-4, wherein said bleach activator is selected from TAED, ISONOBS, NOBS, benzoyl caprolactam and derivatives thereof and benzoyloxybenzene- -sulphonate and mixtures thereof.

6-A perfumed bleaching composition according to any one of Claims 1-5, wherein said bleach activator further comprises a coating material selected from a mixture of alkali metal C₈-C₂₂ fatty acid salt admixed with the corresponding fatty acid, a coating of C₁₄-C₁₈ fatty acids, a mixture of C₁₂-C₁₄ fatty acids and C₁₀-C₂₀ aliphatic alcohols, and an acid coating.

7-A perfumed bleaching composition according to any one of Claims 1-6, wherein said perfume comprises aroma chemicals selected from
a-primary and secondary alcohols at a level of from 1% to 50% by weight,
b-aliphatic and hydrocinnamic aldehydes at a level of from up to 30% by weight,
c-esters, excluding salicylates, at a level of from 5 to 50% by weight,
d-unsaturated ketones at a level of up to 30% by weight.

8-A perfumed bleaching composition according to any one of Claims 1-7, wherein the total sum of the weights of said aroma chemicals in the perfume is at least 50% by weight of the perfume.

9-A perfumed bleaching composition according to any one of Claims 1-8, wherein said perfume comprises aroma chemicals selected from
a-primary and secondary alcohols at a level of from 20% to 45% by weight,
b-aliphatic and hydrocinnamic aldehydes at a level of from up to 20% by weight,

c-esters, excluding salicylates, at a level of from 10% to 40% by weight,
d-unsaturated ketones at a level of up to 25% by weight.

10-A perfumed bleaching composition according to any one of Claims 1-9, wherein the total sum of the weight of said aroma chemicals in the perfume is at least 80% by weight of the perfume.

11-A perfumed bleaching composition according to any one of Claims 1-10, wherein said perfume comprises aroma chemicals selected from

a-primary and secondary alcohols at a level of from 25% to 35% by weight,

b-aliphatic and hydrocinnamic aldehydes at a level of up to 10% by weight,

c-esters, excluding salicylates, at a level of from 25% to 35% by weight,

d-unsaturated ketones at a level of up to 25% by weight.

12-A perfumed bleaching composition according to any one of Claims 1-11, wherein

a-said primary and secondary alcohols are selected from 3,7-dimethyl-6-octen-1-ol, 3,7-dimethyl-2,6-octadien-1-ol, phenyl ethyl alcohol, 1-pentanol, 3-methyl-5-phenyl, cyclohexyl ethyl alcohol, cyclohexanol, 2-tertiary butyl, 4-methyl-3-decen-5-ol, cyclohexanol, 4-tertiary butyl and 4-iso propyl cyclohexanol,
b-said aliphatic aldehydes are selected from octanal, nonanal, decanal, undecanal, dodecanal, 10-undecenal, 2-methyl undecanal and 2-methyl decanal,

c-hydrocinnamic aldehydes are selected from 2-methyl-3-(4-tertiary butyl phenyl) propanal and 2-methyl-3-(4-iso propyl phenyl) propanal,

d-esters, excluding salicylates, are selected from benzyl acetate, benzyl propionate, phenyl ethyl acetate, citronellyl acetate, geranyl acetate, 2-methyl-3-phenyl-propan-2-yl acetate, 4-tertiary butyl cyclohexyl acetate, 2-tertiary butyl cyclohexyl acetate,

hexahydro-4,7-methano-inden-5-yl acetate, hexahydro-4,7-methano-inden-6-yl acetate, hexahydro-4,7-methano-inden-5-yl propionate, hexahydro-4,7-methano-inden-6-yl propionate and methyl benzoate,

e-unsaturated ketones are selected from 7-acetyl

1,2,3,4,5,6,7,8-octahydro 1,1,6,7 tetra methyl naphthalene, 3-buten-2-one 3-methyl-4-(2,6,6, trimethyl-2- cyclohexen-1-yl), 3-buten-2-one 4-(2,6,6-trimethyl-1-cyclohexen-1-yl), 3-buten-2-one 4-(2,6,6-trimethyl-2-cyclohexen-1-yl) and ketone cedr-8-enyl methyl.

13-A perfumed bleaching composition according to any one of Claim 1-12 wherein said bleaching composition further comprises from 0.1 % to 10%, preferably 0.1 % to 3.0% by weight of a chelant selected from aminocarboxylates and aminophosphonates compounds.

14-A perfumed bleaching composition according to any one of Claims 1-13, wherein said chelant is ethylenediamine disuccinate (EDDS).

15-A perfumed bleaching composition according to any one of Claims 1-14, wherein said perfume is incorporated by any means in a composition selected from:

- i)-the bleaching composition as a finished product,
 - ii)-the bleaching composition during its making process,
- or any mixtures thereof.

16-A perfumed bleaching composition according to any one of Claims 1-15, wherein the bleaching composition is in the granular form and has a bulk density of at least 450 g/litre.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/16249

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : 252/95, 174.11, 186.25, 186.38

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/95, 174.11, 186.25, 186.38, 186.39, 186.22, 186.23, 186.26, 186.27, 186.3, 186.31

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|---|-----------------------|
| X | US, A, 4,818,425 (MEIJER ET AL.) 04 April 1989, see the abstract, column 5, lines 21-39, and example 8. | 1-3 |
| X | US, A, 5,332,518 (KURODA ET AL.) 26 July 1994, see the abstract, column 9, lines 34-61, column 11, lines 33-36, and examples 39-42. | 1-3 |
| Y | US, A, 5,258,133 (CHAPPLE) 02 November 1993, see the abstract, column 2, line 50 to column 3, line 10, and the examples. | 1-3 |
| X,E | US, A, 5,482,642 (AGAR ET AL.) 09 January 1996, see the abstract, and example 1. | 1-3 |
| X,P | US, A, 5,411,673 (AGAR ET AL.) 02 May 1995, see the abstract, examples, and claims 1-12. | 1-3 |

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

| | | |
|---|-----|--|
| * Special categories of cited documents: | *T | later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principles or theory underlying the invention |
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Date of the actual completion of the international search

04 APRIL 1996

Date of mailing of the international search report

16 APR 1996

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

JOSEPH D. ANTHONY

Telephone No. (703) 308-1235

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/16249

A. CLASSIFICATION OF SUBJECT MATTER:
IPC (6):

C11D 3/39, 3/50; C01B 15/04, 15/055

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